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13. ABSTRACT (Maximum 200 Words) This project is designed to evaluate the feasibility of using a membrane-supported extraction and biotreatment process to meet NESHAP standards for aircraft painting and depainting facilities. The proposed system will both minimize the treated volume and concentrate the VOCs within that treated volume to further reduce the size and cost of the control equipment. These advantages make this VOC treatment option viable over a broad range of spray booth sizes. This will be accomplished using the partitioned recirculation flow reduction technique and a novel VOC concentrating and biological treatment process, the Membrane BioTreatment (MBT) system.				
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Membrane-Mediated Extraction and Biodegradation of VOCs from Air

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PROJECT BACKGROUND

This project is sponsored by the Strategic Environmental Research & Development Program (SERDP) in response to the Compliance New Start Number 2 Statement of Need (CPSON2) for FY98, entitled, "VOC (Volatile Organic Compound) Control Technology for Aircraft Painting and Depainting Facilities." Driven by the Clean Air Act Amendments of 1990, quantities of VOCs and Hazardous Air Pollutants (HAPs) in coatings are being reduced, thereby reducing emissions of ozone precursors and toxic compounds from painting operations. However, additional controls are desirable or necessary to meet corrosion specifications in some instances, such as aircraft coating. The National Emissions Standard for Hazardous Air Pollutants (NESHAP) specific to aircraft painting will require the Department of Defense (DoD) to either implement volatile hazardous air pollutant (VHAP) control technology or replace existing coating formulations. Because efforts to develop replacement coatings have met with only mixed success, implementation of control technology appears to be the most promising near-term solution.

Project Description

This project is designed to evaluate the feasibility of using a membrane-supported extraction and biotreatment process to meet NESHAP standards for aircraft painting and depainting facilities. The proposed system will both minimize the treated volume and concentrate the VOCs within that treated volume to further reduce the size and cost of the control equipment. These advantages make this VOC treatment option viable over a broad range of spray booth sizes. This will be accomplished using the partitioned recirculation flow reduction technique and a novel VOC concentrating and biological treatment process, the Membrane BioTreatment (MBT) system.

In the MBT system, VOCs are first separated from the air stream, concentrated, then metabolized by microorganisms, forming nonhazardous cell mass and carbon dioxide (CO_2). Selective removal and concentration of VOCs from the exhaust stream enable significant reduction in the volume directed to the final control device. The system allows for independent optimization of each process: VOC removal from the air and VOC biodegradation. The system uses microporous hollow fiber membrane contactors to mediate the extraction and concentration of VOCs from the air into an organic stripping fluid (octanol) and to provide a physical support for degradative microorganisms. Figure 1 is a schematic of the MBT system.

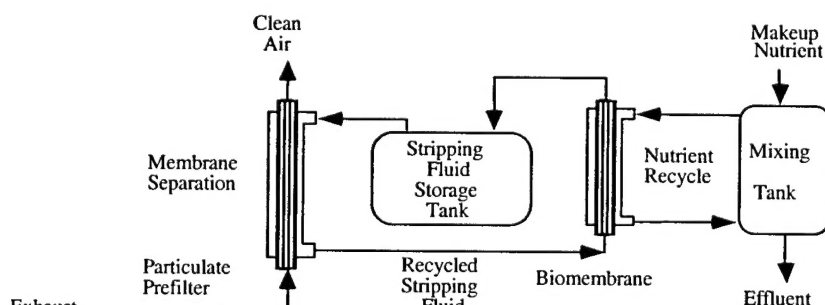


Figure 1: MBT System Schematic

Gases enter a membrane separation/concentration (S/C) unit containing bundles of microporous hydrophobic fibers in which vaporized HAPs and VOCs are transferred into a stripping fluid medium as shown in Figure 2 (dark particles are VOCs). The medium serves as a pollutant sink and allows accumulation of significant HAP/VOC concentrations.

Upon exiting the S/C unit, the stripping fluid is delivered to a biomembrane unit. There, the stripping fluid is circulated past one side of another microporous membrane with VOC-degrading bacteria in a film on the opposite side of the membrane. VOCs diffuse through the membrane pores (filled with organic stripping fluid) and are

selectively metabolized by the bacteria, as shown in Figure 3. The solvent is then collected in a storage vessel, and recycled through the S/C unit. Outputs from the overall MBT system are clean air, CO₂, and a mixture of water and nonhazardous cell mass.

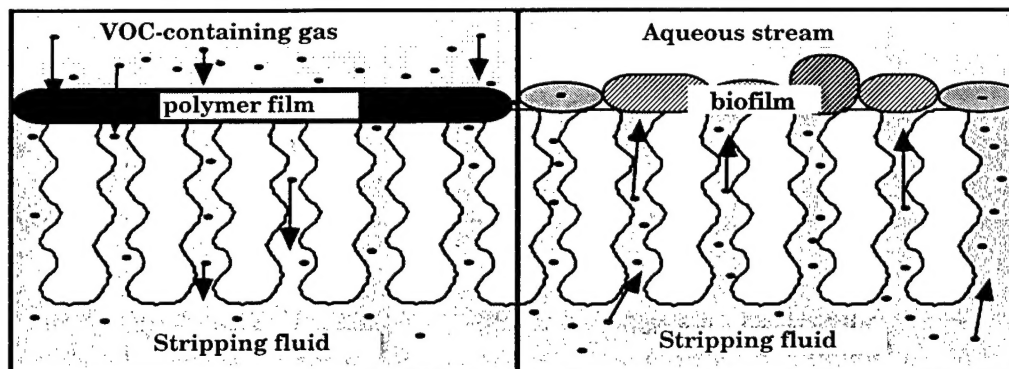


Figure 2: VOC Extraction in the S/C Unit

Figure 3: Bioextraction of VOCs

Separation/Concentration Experiments

Initial evaluations of mass transfer coefficients for the membrane module were conducted by quantifying the removal of each individual VOC [*m*-xylene, toluene, methyl ethyl ketone (MEK)] from an air stream. Experiments were performed to determine the effect of airflow rate, stripping fluid flow rate, air stream VOC concentration, and stripping fluid VOC concentration on overall mass transfer coefficients. Inlet air stream concentrations were set in the range of 50 to 350 ppm on a mole per mole basis with a syringe infusion pump. Airflow rates between 1 and 5 ft³/min (28 and 140 L/min) and stripping fluid flow rates between 0.1 and 1.0 L/min were studied. Contact times for both streams were calculated based on the geometry of the membrane unit. The air-side contact time was 0.1 – 0.4 sec, and the stripping fluid contact time ranged from 6 to 60 sec. Samples of inlet air, outlet air, and the stripping fluid reservoir were taken at regular intervals and analyzed to allow calculation of the overall mass transfer coefficient via an appropriate design equation for the membrane contactor. Air samples were collected and analyzed by gas chromatography using a flame ionization detector (GC/FID) immediately after they were withdrawn from the sample port. Stripping fluid samples were placed into 1.5-mL polypropylene microcentrifuge tubes and stored headspace-free in a -20°C freezer until analysis by ultraviolet - visible (UV-Vis) spectrophotometry or high-pressure liquid chromatography (HPLC) with a UV or refractive index (RI) detector.

Significant effort was aimed at testing the performance and ease of application of several coatings on smaller bench-scale Celgard contactors. We acquired and tested a module from Compact Membrane Systems (CMS) with an amorphous copolymer of perfluorodimethyldioxole and tetrafluoroethylene (PDD-TFE) coating inside the fibers. While it was known that PDD-TFE would not have optimum transfer characteristics, it was the only material that CMS, the only vendor identified and judged at that time to be capable of applying in-situ coatings inside the fibers, would provide. MEK and *m*-xylene were the VOCs used in the VOC mass transfer performance (air to octanol) tests. Three conditions were examined for each compound, in duplicate, for a total of 12 experiments. Airflow rate and VOC concentration were experimental variables, while absorbent (octanol) flow was held constant. Experimental conditions were chosen to emulate previous work with a Celgard Liqui-Cel module containing hollow fibers coated on the outside surface with PDD-TFE. Replicates were not evaluated because the VOC concentration in the solvent varied with time. Efforts were made to duplicate air and solvent flow rates, and VOC concentrations in the air stream. The results of the testing were similar to those of previous testing using a module coated with PDD-TFE on the outside of the

fibers. These results, shown in Table 1, indicate that, with PDD-TFE coated fibers, the major resistance to mass transfer may be in the coating. Table 2 shows the removal efficiencies obtained using PDD-TFE coating on the outside of the fibers. Because PDD-TFE has a relatively high resistance to mass transfer of VOCs, the need for a better polymeric coating to improve process economics is indicated.

Table 1. Mass Transfer Coefficients

PDD-coated membranes, shell-side (outside) coating					
Compound transferred	Air Stream			Solvent Stream	
	Concentration (ppm)	Flow (L/min)	Loading ¹ (ppm/s)	Conc. (mg/L)	K_o ($\times 10^{-5}$ cm/s)
<i>m</i> -xylene	44	28	120	6.2	0.85
	50		130	6.2	0.91
	110	28	290	6.2	0.96
				6.0	1.0
	64	60	370	6.3	1.3
MEK	275		1600	5.9	1.6
	270	28	720	550	0.7
	750	28	2000	105	2.0
	1050	60	6000	1200	9.4
	2200	30	5500	980	4.3
PDD-coated membranes, tube-side (inside) coating					
<i>m</i> -xylene	40	28	110	4080	0.1
	230	60	1300	4300	2.0
	280	60	1600	850	2.7
MEK	470	28	1300	8500	-4.0
	2800	60	16000	9500	2.0
	5000	28	13000	5500	5.3

¹Indicates the relative rate of flow of VOC through the module; determined by dividing the VOC concentration by the residence time of the air in the module (shell-side volume = 175 mL).

Table 2. Removal Efficiencies

PDD-coated membranes, shell-side coating				
Compound transferred	Air Concentration (ppm)	Airflow (L/min)	Loading (ppm/s)	Removal Efficiency (%)
toluene	800	105	8000	74
	900	60	5100	76
	1300	30	3700	78
MEK/toluene	500/250	60	2800/1400	80/60
	850/650	30	2400/1900	80/70

Operating equations were derived to describe the membrane separation processes. The final result for the separation/concentration unit was a design equation that relates concentration, partition coefficient, membrane surface area, and flow rate to an overall mass transfer coefficient, K_o . The K_o is based on the overall system driving force and is defined by a sum of resistances model. In the equation shown below for K_o in the S/C unit, the concentration (C) subscripts A and O denote the air and octanol phases, and subscripts 1 and 2 represent inlet and outlet conditions, respectively. P is the air/octanol equilibrium partition coefficient, Q is the volumetric flow of the respective phases [cm^3/sec], and A_m is the membrane surface area [cm^2].

$$K_o = \frac{\ln \left[\frac{C_{A2}/P - C_{O2}}{C_{A1}/P - C_{O1}} \right]}{A_m \left(\frac{1}{Q_o} - \frac{1}{Q_A P} \right)}$$

Module design

Discussions were held with Applied Membrane Technologies (AMT) regarding their standard parallel flow, stainless steel cylindrical module and potential designs for improving the air distribution and reducing air-side pressure drop. AMT was contracted to deliver a membrane module using fibers that are coated on the outside with plasma-polymerized silicone rubber at a nominal thickness of 1 μm . One of the concerns with a parallel-flow contactor design is the unknown effectiveness of the air-to-fiber contact area. Though the cylindrical parallel-flow design of the existing AMT module does not lend itself to high efficiency, it was used in preliminary testing to gather data for the design of a cross-flow bench-scale module.

Five 48-minute tests were conducted with air flowing through the shell side of the module, three using *m*-xylene as the pollutant and two with MEK. Results are presented in Table 3. The air flow was typically 60 L/min and VOC removal ranged from 56 to 83 percent with average overall mass transfer coefficients, K_o , of 4.4×10^{-6} to 5.0×10^{-5} cm/sec.

Table 3. Air in Shell Tests – Cylindrical Parallel-flow AMT Module

Parameter					
Run ID	<i>m</i> -xylene 1	<i>m</i> -xylene 2	<i>m</i> -xylene 3	MEK 1	MEK 2
Total run time (min)	48	48	48	48	48
Airflow (L/min)	60	60	60	28	60
Avg inlet VOC air concentration (molar ppm)	65	190	185	186	1350
Average VOC removal (%)	56	77	70	83	78
Average mass transfer coefficient, K_o (cm/s)	4.40E-06	8.30E-06	1.20E-05	2.10E-05	5.00E-05

In actual operation, contaminated air flows through the shell side of a cylindrical design and octanol, or another stripping fluid, is pumped through the tube, or lumen side. The initial set of tests on the AMT cylindrical module was run in this manner. Because of the distribution and contact shortcomings encountered, AMT suggested that a second series of tests be conducted with the air flowing through the fibers. Therefore, a second set of tests was run with the air flowing through the fibers and octanol on the shell side. Twelve runs were conducted using *m*-xylene as the pollutant. These shorter (34 min) tests were conducted with airflow rates through the lumens ranging from 5.6 to 10.3 L/min at pressure drops from 11.5 to 20 in. H_2O (292 – 508 mm/ H_2O). Results are shown in Table 4.

Table 4. Octanol in Shell Tests – Cylindrical Parallel-flow AMT Module

Parameter												
Run ID	<i>m</i> -xylene 7	<i>m</i> -xylene 8	<i>m</i> -xylene 9	<i>m</i> -xylene 10	<i>m</i> -xylene 11	<i>m</i> -xylene 12	<i>m</i> -xylene 13	<i>m</i> -xylene 14	<i>m</i> -xylene 15	<i>m</i> -xylene 16	<i>m</i> -xylene 17	<i>m</i> -xylene 18
Total run time (min)	34	34	34	34	34	34	34	34	34	34	34	34
Air-side Pressure Drop in. H_2O (mm/ H_2O)	11.5 (292)	11.0 (279)	11.5 (292)	11.0 (279)	16.0 (406)	16.0 (406)	16.5 (419)	16.0 (406)	20.0 (508)	20.0 (508)	20.0 (508)	20.0 (508)
Air flow (L/min)	5.6	5.6	5.6	5.6	8.6	8.6	8.6	8.6	10.3	10.3	10.3	10.3
Avg inlet VOC air concentration (molar ppm)	68	84	261	684	92	125	457	499	76	105	274	697
Average VOC removal (%)	91	91	80	97	51	44	93	89	60	52	73	85
Average mass transfer	1.60E-06	1.90E-06	8.20E-07	2.30E-06	8.60E-07	6.00E-07	3.60E-06	2.50E-06	5.10E-06	1.20E-06	1.60E-06	2.00E-06

Figure 4. Flat-sheet biofilm reactor

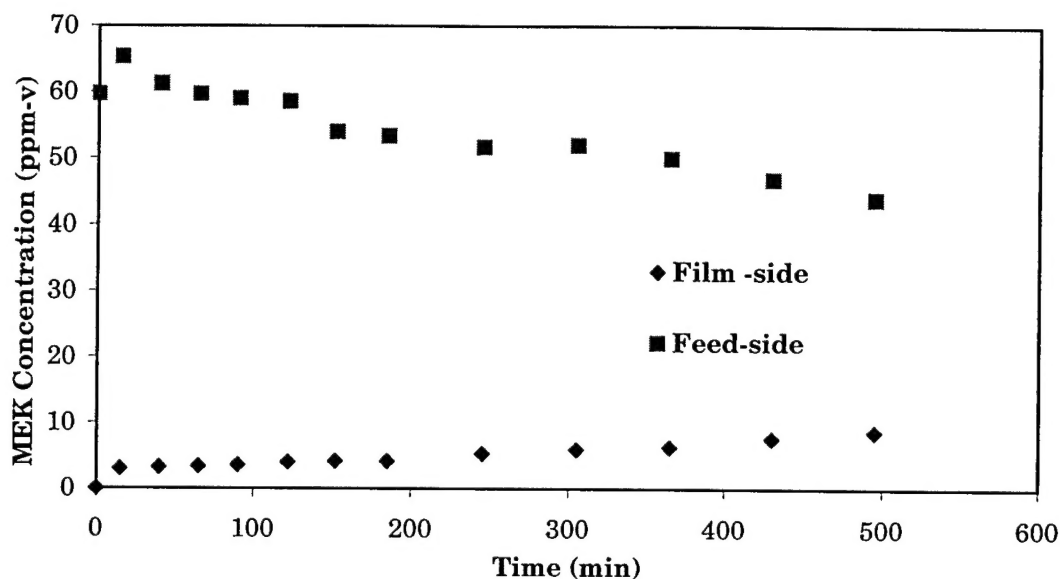


Figure 5. M-1 biofilm degradation of MEK in aqueous/octanol system

A biofilm containing an MEK-degrading bacteria (M-1) was established. Octanol containing MEK was present on the feed side of the membrane. Water and octanol were recirculated between the membrane module and equally sized reservoirs. As indicated in Figure 5, the concentrations of MEK in the octanol phase decreased more rapidly than the aqueous-phase MEK concentration increased. Consistent biodegradation of MEK occurred over the course of a 9-hour period, following transfer of MEK from the octanol across the membrane to the biofilm. This proved that transfer with biodegradation would occur under conditions where the organisms were in close contact with octanol. It also indicated that while M-1 would grow, slowly utilizing octanol as a carbon source (data not shown), octanol metabolism would not severely inhibit MEK degradation.

M-1 was grown in a film and exposed to a mixture of MEK and toluene in water on the feed side. The concentration of MEK in the feed stream was at 25 ppm through day 5, then increased to 50 ppm through day 25, when it was again decreased to 25 ppm. The toluene concentration in the feed was zero until day 25, when it was increased to 25 ppm. Despite prior growth on MEK, the film rapidly degraded a substantial portion of the toluene fed, decreasing the rate of MEK degradation in the process. This result was surprising, due to the fact that M-1 is an organism isolated from soil using MEK as the enrichment carbon source. However, since the soil was subjected to long-term exposure to motor fuels, toluene degradation is to be expected.

A biofilm, containing both M-1 and an *m*-xylene degrading bacteria (X-1), was established and fed toluene and MEK in an aqueous mixture, each at a concentration of 50 ppm in the feed stream. After 2 hours of continuous flow, sampling was begun. Toluene was rapidly and almost completely degraded, while MEK was degraded to a significantly lesser extent. This suggests that both M-1 and X-1 preferentially degrade toluene, to the detriment of MEK degradation.

A biofilm containing M-1 and X-1 was exposed to an octanol feed mixture containing 50 ppm each of MEK and toluene. The octanol flow rate was 2 mL/min, while the aqueous flow rate was 7 mL/min. Toluene did not appear in the aqueous stream over the course of the experiment. Essentially all of the toluene was degraded, as was one-third of the MEK (data not shown).

A mixed organism biofilm culture containing M-1 and X-1 was fed a mixture of MEK, toluene, and *m*-xylene from an aqueous stream (50 ppm of each compound). The culture's behavior and VOC removal capability were investigated, and results are shown in Figure 6. Neither toluene nor *m*-xylene appeared in the aqueous phase, and MEK appeared at low levels (<5 ppm).

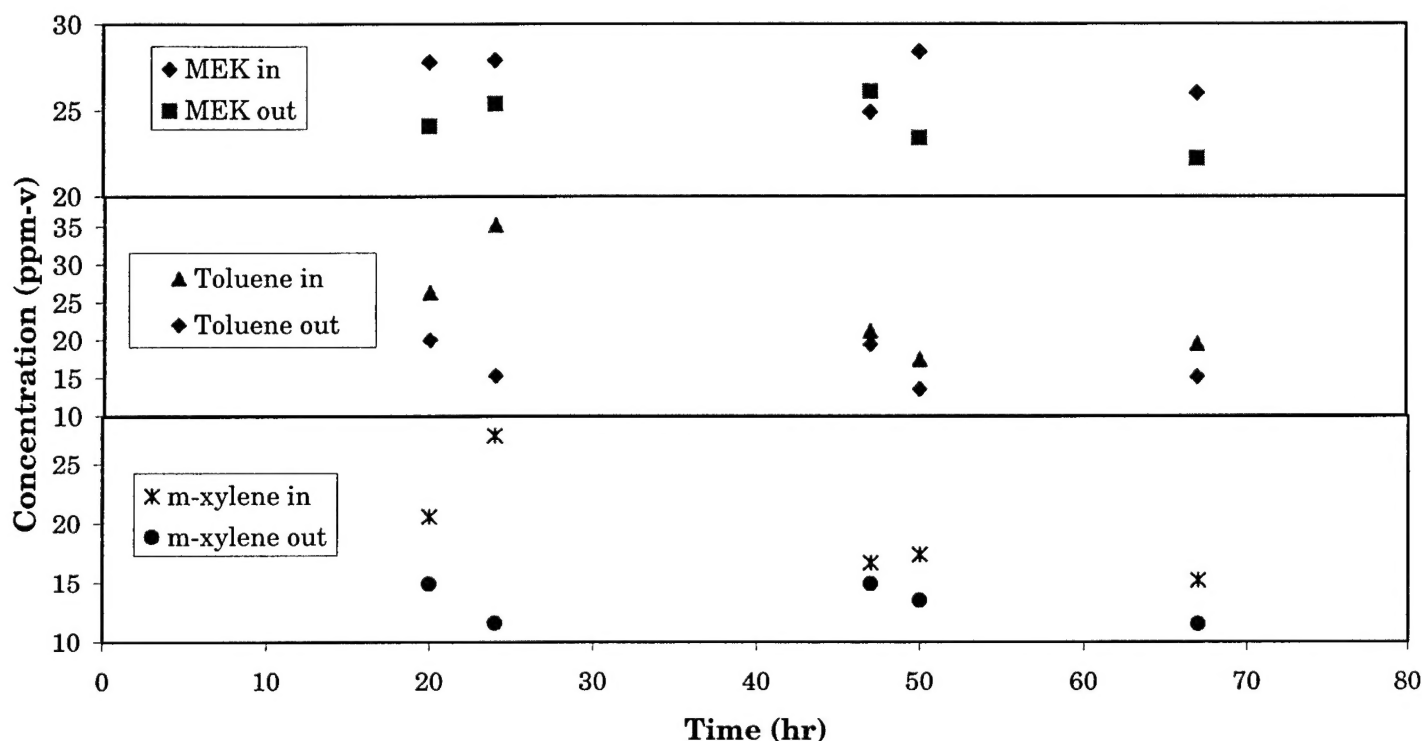


Figure 6. M-1 and X-1 mixed biofilm degradation of MEK, toluene, and *m*-xylene

These results have significant implications for the design and operation of the biotreatment system. For example, since M-1 preferentially degrades toluene over MEK, a single biofilm module may be inadequate. Several strategies may need to be evaluated, including replacement of M-1 with an organism exhibiting higher substrate specificity for MEK, establishment of an MEK-degrading culture in the aqueous recirculation tank, or staging of biofilm modules containing different bacterial populations. The mixed culture results are more difficult to analyze. It may have been that X-1 dominated the biofilm and that the low MEK degradation rates are attributable to low population size for M-1. Such issues must be investigated more completely.

Shake flask results

The apparent inhibition of MEK degradation by toluene and *m*-xylene was investigated in a series of shake flask experiments. MEK and *m*-xylene/toluene have different solubilities in an aqueous medium. Under certain conditions in the biofilm reactor, MEK from the octanol phase will partition into the aqueous nutrient medium faster than it can be degraded by the biofilm. This will result in exposure of the biofilm to an aqueous-phase MEK concentration. The biofilm must be able to maintain degradative activity in the presence of this aqueous-phase MEK. The film must also actively degrade MEK. Given the results obtained from the biofilm experiments, suspended cell studies were undertaken to further elucidate the mechanisms of degradation of the two organisms.

X-1 was grown on toluene and *m*-xylene, to determine its substrate preference. As indicated in Figure 7, only one apparent growth phase results, suggesting that toluene and *m*-xylene are equally preferred and that degradation of either does not inhibit degradation of the other.

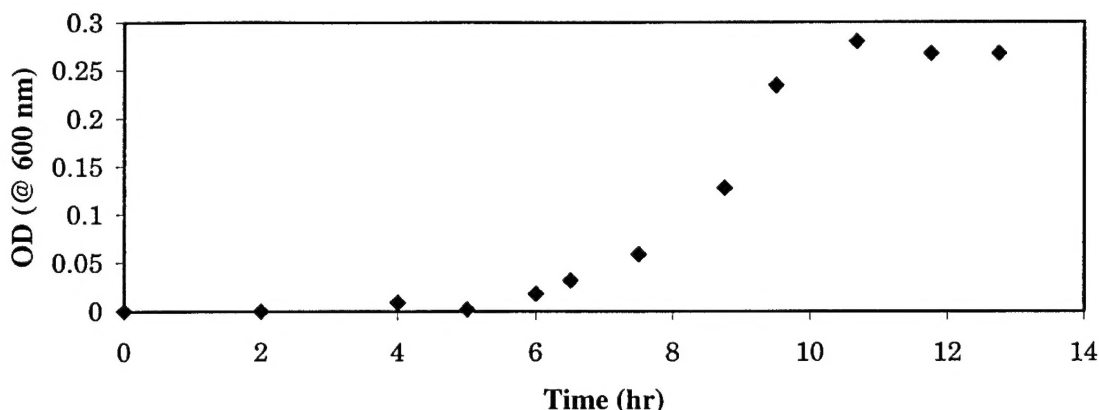


Figure 7. X-1 growth on toluene and *m*-xylene

Growth studies of M-1 were performed with various mixtures of MEK, toluene, and *m*-xylene. The cell density, protein concentration, and concentration of the three substrates were monitored during the growth. The results of these studies are summarized in Table 6. Since multiple growth phases were observed, multiple growth rates are reported, with the primary carbon source denoted in parentheses. These results indicate that M-1 degrades toluene and *m*-xylene preferentially to MEK, and that the growth rate of M-1 on MEK is reduced as a result of toluene and *m*-xylene metabolism. It is unclear whether inhibitory byproducts are formed by M-1 during aromatic biodegradation.

Table 6. Growth of M-1 on Mixed Substrates

Substrate	Specific Growth Rate (h ⁻¹)	Growth patterns
MEK (200 ppm) + toluene (25 ppm)	0.35 (toluene) 0.22 (MEK)	sequential phases consuming toluene, then MEK
MEK (60 ppm) + <i>m</i> -xylene (35 ppm)	0.45 (<i>m</i> -xylene) 0.11 (MEK)	sequential phases consuming <i>m</i> -xylene, then MEK

FUTURE APPROACH

We are evaluating the mass transfer characteristics of bench-scale modules using single-component air streams containing MEK, *m*-xylene, and toluene at concentrations varying from 50 to 200 ppm. Octanol has been used as the VOC stripping fluid, but it has been found to swell the fibers. As a consequence, silicone oil, which does not cause the fibers to swell, is the current transfer fluid of choice. Experiments will be performed to determine the effect of airflow rates, stripping fluid flow rate, air stream VOC concentration, and stripping fluid VOC concentration on the overall mass transfer coefficient using silicone oil. Work will continue in evaluating the mass transfer rates of various VOC mixtures including binary and tertiary mixtures at total VOC levels from 50 to 300 ppm. Preliminary targets for mass transfer rates for removing VOCs from air and VOC degradation rates are 10^{-5} cm/sec and 3×10^{-10} mg/cell-hr, respectively.

It is necessary to operate a biofilm reactor for 2 to 3 months in order to determine the effectiveness of the degradative mixed culture. During this period, the aqueous-phase pressure drop, the cell mass sloughing rate, and the biodegradation rate will be monitored. These variables will enable calculation of the effectiveness of the biotreatment module for degradation of specific VOCs, and will provide valuable insight into the extent to which biofouling might occur and the severity of the impact of biofouling on degradative performance.

SUMMARY

VOC removal efficiencies in excess of 75% have been achieved using a microporous hollow fiber membrane module. This module was coated on the air-contacting side with either PDD-TFE or plasma-polymerized silicone rubber. The VOC-laden air had a contact time of less than 0.1 sec with the coated membrane. Operation of these modules was not optimized, and removal efficiencies in excess of 90% have been observed. Extraction of

specific compounds from the air stream into octanol was observed to be unaffected by the presence or concentration of other VOCs in the air stream, but extraction increased with VOC concentration in the air stream.

The membrane-supported biofilm modules successfully removed VOCs from the recirculating octanol stream. Degradation of the aromatic compounds investigated (toluene, *m*-xylene) was achieved; these compounds were not observed in the aqueous phase above the biofilm. MEK biodegradation is problematic, appearing to be partially inhibited by toluene and *m*-xylene. Further mechanistic studies are required to ascertain the underlying mechanism.

Overall, the MBT process continues to exhibit the potential for development into a robust, flexible, low-cost treatment system suitable for implementation at facilities subject to the NESHAP for Aerospace Manufacturing and Rework Facilities.